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Process for the Production of a Thermoplastic Polyester

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(54) [Title of the Invention] **Process for the Production of a Thermoplastic Polyester**

(57) [Summary]

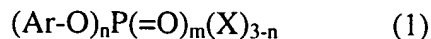
[Object] To provide a process capable of efficiently manufacturing a thermoplastic polyester with a very low content of terminal carboxyl groups and excellent resistance to hydrolysis.

[Means of Achievement] A thermoplastic polyester is produced by conducting an esterification or transesterification reaction in the presence of a metal catalyst, followed by a polycondensation reaction, wherein 2-50 mmol/kg of a nitrogen-containing organic base is added to the thermoplastic polyester at any stage of the reaction, and 2-50 mmol/kg of a specific organic phosphorus compound is added to the thermoplastic polyester during the polycondensation reaction.

[Claims]

[Claim 1] A process for the production of a thermoplastic polyester with few terminal carboxyl groups by conducting an esterification reaction or transesterification reaction in the presence of a metal catalyst, and then conducting a polycondensation reaction, wherein a nitrogen-containing

organic base is added in an amount of 2-50 mmol/kg with respect to the thermoplastic polyester at any stage of the reaction, and an organic phosphorus compound shown by general formula (1) below is further added in an amount of 2-50 mmol/kg with respect to the thermoplastic polyester during the polycondensation reaction.



[where m is 0 or 1; n is an integer of from 1 to 3; Ar is an aryl group; X is a hydrogen atom, hydroxyl group, hydrocarbon group, or halogen atom; and each may be the same or different.]

[Claim 2] The process for the production of a thermoplastic polyester according to Claim 1, wherein the aforementioned organic phosphorus compound is added at an arbitrary point in time once the intrinsic viscosity of the polyester has reached 0.3 dL/g or higher due to the polycondensation reaction.

[Claim 3] The process for the production of a thermoplastic polyester according to Claims 1 or 2, wherein the polycondensation reaction subsequent to addition of the organic phosphorus compound is carried out by melt extrusion in an extruder.

[Claim 4] The process for the production of a thermoplastic polyester according to any of the Claims 1-3, wherein the thermoplastic polyester is produced from a glycol and a dicarboxylic acid or an ester-forming derivative thereof.

[Claim 5] The process for the production of a thermoplastic polyester according to any of the Claims 1-3, wherein the thermoplastic polyester is produced from an aliphatic glycol and an aromatic dicarboxylic acid or an ester-forming derivative thereof.

[Claim 6] The process for the production of a thermoplastic polyester according to any of the Claims 1-5, wherein the nitrogen-containing organic base is a tertiary amine.

[Claim 7] The process for the production of a thermoplastic polyester according to any of the Claims 1-5, wherein the nitrogen-containing organic base is a tertiary amine with a heterocyclic structure.

[Claim 8] The process for the production of a thermoplastic polyester according to any of the Claims 1-7, wherein the Ar (aryl group) in general formula (1) is a phenyl group.

[Detailed Description of the Invention]

[0001]

[Technological Field of the Invention] The present invention relates to a process for the production of thermoplastic polyester. More specifically, it relates to a process that makes it

possible to efficiently produce a thermoplastic polyester with few terminal carboxyl groups in the polymer and excellent resistance to hydrolysis in a short reaction time.

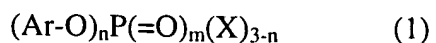
[0002]

[Prior Art, and Problems That the Invention Is Intended to Solve] Thermoplastic polyesters such as polyalkylene terephthalate resins and polyalkylene naphthalate resins are used for a wide range of purposes such as fibers, films, and other various types of molded goods because of their excellent physical properties (mechanical properties, electrical properties, and the like), chemical properties, and processability. On the other hand, hydrolysis lowers the physical properties of thermoplastic polyester resins relatively easily because the main chain of such resins contains ester bonds. It is known that the lower the concentration of terminal carboxyl groups in the polymer, the greater the improvement is in this deterioration by hydrolysis. Many studies have consequently been conducted on the catalysts and stabilizers that are used in polymer production in order to decrease the number of such terminal carboxyl groups. Studies have also been conducted regarding end-capping agents, coupling agents, and other compounds designed to consume the terminal carboxyl groups. Devising new catalysts and stabilizers has some degree of effect in lowering the number of terminal carboxyl groups by inhibiting thermal deterioration during polymerization, but does not achieve a great reduction. Even though end-capping agents and coupling agents have a significant effect, they have many drawbacks, such as causing problems with the uniformity of the reaction since they are generally used in the polymerization reaction, the risk of inducing secondary reactions depending on the compound used, and having drawbacks in terms of reaction control. Melt polycondensation is the most common industrial process for obtaining thermoplastic polyesters. In this process, a homogeneous solution-phase system is heated to or above the melting point of the monomers and the polymer, and reactions are performed in the system with consideration for economic efficiency and monomer availability. However, many undesirable secondary reactions progress during production because the polymer is exposed for a long period of time to a high temperature (at or about the melting point) under a high vacuum in melt polycondensation. For example, undesirable terminal groups (such as carboxyl groups) are produced by the thermal decomposition or hydrolysis of the main chain and the terminals, and undesirable low molecular weight components (such as acetaldehyde, tetrahydrofuran, and terephthalic acid) are generated in association with the degradation reactions. The most important among these are the reactions that generate terminal

carboxyl groups. The terminal carboxyl groups greatly affect the quality of the polyester resin. As the secondary reactions, including those that produce terminal carboxyl groups, become more prominent, the quality of the polyester resin thus obtained, such as its resistance to hydrolysis, heat resistance, bleed resistance, and mechanical properties, declines. The most effective means of suppressing such secondary reactions is to make the reaction time as short as possible. Catalysts and additives have consequently been studied, as was mentioned above. Nonetheless, their effects have been inadequate. On the other hand, there are limits to the molecular weight of the polyester obtained by such melt polycondensation. Solid-phase polymerization has been used for some time to obtain a higher molecular weight. Solid-phase polymerization involves polycondensation in solid form in an inert gas stream or in a vacuum at a temperature at or below the melting point of the polymer. This inevitably leads to much higher costs because it necessitates a new process and requires a longer reaction at a lower reaction rate than does melt polycondensation.

[0003]

[Means Used to Solve the Above-Mentioned Problems] As a result of studies conducted to resolve the above problems and to provide a process for the production of a thermoplastic polyester whereby the number of terminal carboxyl groups in the polymer is reduced, excellent resistance to hydrolysis is obtained, the reaction time is shortened, and the molecular weight of the resulting polymer is raised, the present inventors discovered unexpectedly that the terminal carboxyl groups of the thermoplastic polyester can be significantly reduced and the polycondensation reaction markedly accelerated by adding a nitrogen-containing organic base and a certain type of phosphorus compound in addition to the usual thermoplastic polyester polycondensation catalyst, and perfected the present invention. Specifically, the present invention relates to a process for the production of a thermoplastic polyester with few terminal carboxyl groups by conducting an esterification or transesterification reaction in the presence of a metal catalyst, and then conducting a polycondensation reaction, characterized in that a nitrogen-containing organic base is added in an amount of 2-50 mmol/kg with respect to the thermoplastic polyester at any stage of the reaction, and an organic phosphorus compound shown by general formula (1) below is further added in an amount of 2-50 mmol/kg with respect to the thermoplastic polyester during the polycondensation reaction.



[where m is 0 or 1; n is an integer of from 1 to 3; Ar is an aryl group; X is a hydrogen atom, hydroxyl group, hydrocarbon group, or halogen atom; and each may be the same or different.]

[0004]

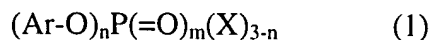
[Embodiments of the Invention] The present invention will be explained in detail below. The term "thermoplastic polyester" in the present invention means a polymer that contains ester bonds and is produced by polycondensing a diol and a dicarboxylic acid or an ester-forming derivative thereof, polycondensing a hydroxy acid or an ester-forming derivative thereof, or polycondensing a hydroxy acid or an ester-forming derivative thereof, a dicarboxylic acid or an ester-forming derivative thereof, and a diol. Examples of the dicarboxylic acids and ester-forming derivatives thereof that can be used herein include aromatic dicarboxylic acids, alicyclic dicarboxylic acids, aliphatic dicarboxylic acids, heterocyclic dicarboxylic acids, polyfunctional carboxylic acids, and ester-forming derivatives of these, such as alkyl esters, phenyl esters, and acylated forms of the aforementioned carboxylic acids. Concrete examples include terephthalic acid, isophthalic acid, phthalic acid, naphthalenedicarboxylic acid, biphenyldicarboxylic acid, stilbenedicarboxylic acid, 2,2-(biscarboxyphenyl)propane, biscarboxyphenylsulfone, cyclohexanedicarboxylic acid, succinic acid, adipic acid, sebacic acid, dodecanedioic acid, dimer acid, pyridinedicarboxylic acid, trimellitic acid, trimesic acid, pyromellitic acid, and ester-forming derivatives of these. One type may be used, or two or more types may be used in mixture form. Examples of diols include ethylene glycol, 1,3-propandiol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, diethylene glycol, triethylene glycol, hydroquinone, bisphenol A, bisphenol S, biphenol, 2,2-(bishydroxyethoxyphenyl)propane, bishydroxyethoxyphenylsulfone, 4,4'-bis(hydroxyethoxy)biphenyl, dimer diol, polyethylene glycol, polytetramethylene glycol, trimethylol propane, and pentaerythritol. Examples of hydroxy acids include hydroxybenzoic acid, hydroxynaphthoic acid, 4-hydroxy-4'-carboxybiphenyl, and ester-forming derivatives of these. One type can be used, or two or more types can be used in mixture form. Especially preferred among the aforementioned thermoplastic polyesters for the application of the present invention are thermoplastic polyesters produced from a glycol and a dicarboxylic acid or an ester-forming derivative thereof. More preferred are thermoplastic polyesters produced from an aliphatic glycol and an aromatic dicarboxylic acid or an ester-forming derivative thereof; specifically, thermoplastic polyesters

composed mainly of polybutylene terephthalate, polyethylene terephthalate, polycyclohexylene dimethylene terephthalate, polybutylene naphthalate, and polyethylene naphthalate.

[0005] These thermoplastic polyesters are produced by conducting an esterification or transesterification reaction in the presence of a metal catalyst, and then carrying out a polycondensation reaction. Specifically, a thermoplastic polyester precursor is produced by heating such a dicarboxylic acid or an ester-forming derivative thereof, a diol or a derivative thereof, and a hydroxycarboxylic acid or a derivative thereof together with a catalyst in a reactor. The thermoplastic polyester is then produced by conducting a polycondensation reaction while distilling off the excess monomer or extraneous components. The following known compounds generally useful in the production of thermoplastic polyesters may also be used as the metal catalyst, either individually or in combinations of two or more types: tetraalkyl titanates or hydrolysates thereof (such as tetrabutyl titanate and tetraisopropyl titanate); titanium oxalate metal salts such as potassium titanium oxalate; organic tin compounds such as butyltin acid, dibutyltin oxide, and dibutyltin diacetate; acetic acid metal salts such as sodium acetate, potassium acetate, zinc acetate, lead acetate, manganese acetate, and calcium acetate; antimony compounds such as antimony trioxide; and germanium compounds such as germanium oxide. The amount of catalyst used in the present invention, calculated in terms of metal atoms, is preferably 10-2000 ppm with respect to the polymer theoretically produced. A range of 20-1500 ppm is more preferred. The time of addition of the metal catalyst is also not particularly restricted, and the catalyst can be added before or during the esterification or transesterification reaction, or immediately before or during the polycondensation reaction.

[0006] The nitrogen-containing organic base is added at any stage of the reaction in the present invention. Examples of the nitrogen-containing organic base used include monoalkylamines, dialkylamines, trialkylamines, monoarylamines, and heterocyclic bases. Concrete examples include pyrazole, imidazole, N-methylimidazole, N-phenylimidazole, 2-methylimidazole, 2-phenylimidazole, 2-imidazoline, 3-imidazoline, benzoimidazole, N-methylbenzoimidazole, triazoles, benzotriazole, pyridine, picolinic acid, phenylpyridines, bipyridyls, quinolone, isoquinoline, acridine, phenanthrolines, pyridoindoles, naphthyridines, pyridazine, pyrimidine, pyrazine, purine, and triazines. One or two or more nitrogen-containing organic bases selected from among these may be used in a proportion of 2-50 mmol/kg with respect to the weight of the thermoplastic polyester produced in accordance with the present invention. When the amount

added is less than 2 mmol/kg, the addition causes little reduction in the terminal carboxyl groups or acceleration of the polycondensation reaction. When the amount exceeds 50 mmol/kg, secondary reactions and discoloration sometimes become prominent. The addition can be made at any time. For example, it can be made before or during the esterification or transesterification reaction, or immediately before or during the polycondensation reaction. Also, as will be discussed below, it can be added together with the organic phosphorus compound when such a compound is added during melt extrusion. Another feature of the present invention is that it is only when an organic phosphorus compound shown by general formula (1) below is added together with the nitrogen-containing organic base that the target thermoplastic polyester can be obtained and the polycondensation reaction accelerated.



[where m is 0 or 1; n is an integer of from 1 to 3; Ar is an aryl group; X is a hydrogen atom, hydroxyl group, hydrocarbon group, or halogen atom; and each may be the same or different.]

Compounds in which Ar (aryl group) is a phenyl group are preferred among these organic phosphorus compounds. Concrete examples include triphenyl phosphite, diphenyl phosphite, diphenyl ethyl phosphite, diphenyl chlorophosphite, diphenyl ethyl phosphonite, diphenyl phenyl phosphonite, phenyl phosphite, phenyl diethyl phosphite, phenyl dichlorophosphite, phenyl diethyl phosphinite, phenyl diphenyl phosphinite, triphenyl phosphate, diphenyl phosphate, diphenyl ethyl phosphate, diphenyl chlorophosphate, diphenyl ethyl phosphonate, diphenyl phenyl phosphonate, phenyl phosphate, diphenyl diethyl phosphate, phenyl dichlorophosphate, phenyl diethyl phosphinate, and phenyl diphenyl phosphinate. One or two or more types of compounds selected from among these may be added in a proportion of 2-50 mmol/kg with respect to the weight of the thermoplastic polyester to be produced. When the amount added is less than 2 mmol/kg, there is little reduction in the terminal carboxyl groups and little acceleration of the polycondensation reaction. When the amount exceeds 50 mmol/kg, secondary reactions and discoloration sometimes become prominent. The time of addition can be any time during the polycondensation reaction. However, since the phosphorus compounds also lower the activity of the metal catalyst used in the polymerization reaction, it is generally preferable to add them at a point in time when the molecular weight of the thermoplastic polyester has reached a certain level in accordance with the goal when the intention is also to accelerate the polycondensation reaction. Concretely speaking, it is preferable to add them when the intrinsic

viscosity of the polyester has reached 0.3 dL/g or higher. When the compounds are added before this time, acceleration of the reaction after addition becomes inadequate. They can also be added by mixing them with a polyester that has an intrinsic viscosity of 0.3 dL/g or higher and is produced beforehand by melt polymerization and melt extrusion in an extruder. In this case, the polyester added may be one produced with or without adding a nitrogen-containing organic base, but the latter situation requires that the organic phosphorus compound and nitrogen-containing organic base be added simultaneously during extrusion. The content of terminal carboxyl groups in the thermoplastic polyester produced in this way is markedly decreased in comparison to when neither an organic base nor an organic phosphorus compound has been used.

[0007] Suitable thermostabilizers, ultraviolet absorbers, antistatic agents, flame retardants, flame-retardant auxiliaries, colorants such as dyes and pigments, lubricant additives to improve the fluidity and mold release property, lubricants, crystallization accelerators (nucleating agents), inorganic matter, and the like can be used as necessary in the thermoplastic polyester obtained according to the present invention. Other thermoplastic resins can also be used jointly in a supplementary manner with the thermoplastic polyester of the present invention within ranges that do not interfere with the object of the invention. Examples of other thermoplastic resins that can be used herein include polyolefin-based polymers, polyamide-based polymers, polycarbonate, ABS, polyphenylene oxide, polyalkyl acrylates, polyacetal, polysulfone, polyether sulfone, polyether imide, polyether ketone, and fluorocarbon resins. These thermoplastic resins can also be used in mixtures of two or more types.

[0008]

[Working Examples] The present invention is explained more concretely below through working examples. However, the present invention is not limited by these examples. In the working examples below, "parts" means "parts by weight." The content of terminal carboxyl groups (COOH) was determined by dissolving 0.2 g of thermoplastic polyester in 40 mL of a mixture of heated benzyl alcohol and chloroform, and titrating the product with a 0.01-mol/L sodium hydroxide benzyl alcohol solution. The intrinsic viscosity was measured using a 3:2 mixed solvent consisting of phenol and tetrachloroethane.

Working Example 1

One hundred parts of dimethyl terephthalate, 60 parts of 1,4-butanediol, 0.06 part of tetrabutyl titanate, and 0.08 part of imidazole were placed in a reactor equipped with a stirrer, nitrogen inlet pipe, and reflux distillation pipe. Transesterification was carried out while gradually raising the temperature from 140 to 210°C under normal pressure and distilling off the methanol. After then stopping the nitrogen supply, the reactor was placed under vacuum while the temperature was gradually raised to 250°C, and a polycondensation reaction was finally carried out at 13 Pa. The intrinsic viscosity of the polymer reached 0.65 dL/g 80 minutes after the beginning of the vacuum procedure. A quantity of 0.35 part of triphenyl phosphite was added at this time, and a polybutylene terephthalate (PBT) polymer was obtained by stirring under reduced pressure for another five minutes. Table 1 shows the intrinsic viscosity, polycondensation time, and COOH content of the PBT obtained.

Working Example 2

A PBT polymer was produced in the same way as in Working Example 1, except that 0.11 part of imidazole and 0.52 part of triphenyl phosphite were used. Table 1 shows the intrinsic viscosity, polycondensation time, and COOH content of the PBT obtained.

Working Example 3

A PBT polymer was produced in the same way as in Working Example 1, except that 0.23 part of imidazole and 1.1 part of triphenyl phosphite were used, and the imidazole was not supplied with the raw materials but was added simultaneously with the triphenyl phosphite. Table 1 shows the intrinsic viscosity, polycondensation time, and COOH content of the PBT obtained.

Working Example 4

A PBT polymer was produced in the same way as in Working Example 1, except that 0.23 part of imidazole and 1.1 part of triphenyl phosphite were used, and the triphenyl phosphite was added when the intrinsic viscosity of the polymer had reached 0.43 dL/g 50 minutes after the beginning of the vacuum procedure. Table 1 shows the intrinsic viscosity, polycondensation time, and COOH content of the PBT obtained.

Working Examples 5 and 6

PBT polymers were produced in the same way as in Working Example 1, except that 0.09 part of 2-methylimidazole (Working Example 5) or 0.09 part of N-methylimidazole (Working Example 6) was used instead of imidazole. Table 1 shows the intrinsic viscosity, polycondensation time, and COOH content of the PBT obtained.

Working Example 7

A PBT polymer was produced in the same way as in Working Example 3, except that 0.26 part of pyridine was used instead of imidazole and 1.1 part of triphenyl phosphite was used. Table 1 shows the intrinsic viscosity, polycondensation time, and COOH content of the PBT obtained.

Working Examples 8-10

PBT polymers were produced in the same way as in Working Example 1, except that 0.15 part of isoquinoline (Working Example 8), 0.18 part of 2,2-bipyridyl (Working Example 9), or 0.08 part of 1,2,4-triazole (Working Example 10) was used instead of imidazole. Table 1 shows the intrinsic viscosity, polycondensation time, and COOH content of the PBT obtained.

Working Examples 11 and 12

PBT polymers were produced in the same way as in Working Example 1, except that 0.27 part of diphenyl phosphite (Working Example 11) and 0.37 part of triphenyl phosphate (Working Example 12) were used instead of triphenyl phosphite. Table 1 shows the intrinsic viscosity, polycondensation time, and COOH content of the PBT obtained.

Working Example 13

A PBT polymer was produced in the same way as in Working Example 1, except that 0.11 part of n-butylin acid was used as the catalyst instead of tetrabutyl titanate. Table 1 shows the intrinsic viscosity, polycondensation time, and COOH content of the PBT obtained.

[0009] Working Example 14

One hundred parts of bis(2-hydroxyethyl)terephthalate, 0.05 part of imidazole, and 0.04 part of germanium dioxide were placed in the same reactor as in Working Example 1, and the temperature was gradually raised to 240°C under normal pressure. The supply of nitrogen

was stopped, the reactor was then gradually placed under vacuum while raising the temperature to 285°C, and a polycondensation reaction was finally carried out at 13 Pa. The intrinsic viscosity of the polymer reached 0.6 dL/g 70 minutes after the beginning of the vacuum procedure, and 0.23 part of triphenyl phosphite was added at that point in time. A polyethylene terephthalate (PET) polymer was obtained by stirring under reduced pressure for five more minutes. Table 2 shows the intrinsic viscosity, polycondensation time, and COOH content of the PET obtained.

Working Example 15

A PET polymer was obtained in the same way as in Working Example 14, except that 0.04 part of tetrabutyl titanate was used instead of germanium dioxide. Table 2 shows the intrinsic viscosity, polycondensation time, and COOH content of the PET obtained.

Working Example 16

One hundred parts of dimethyl terephthalate, 100 parts of 1,4-cyclohexane dimethanol, 0.08 part of tetrabutyl titanate, and 0.1 part of imidazole were placed in the same reactor as in Working Example 1. Transesterification was carried out while gradually raising the temperature from 140 to 240°C under normal pressure, and the methanol was distilled off. The supply of nitrogen was stopped, the reactor was then placed under vacuum while the temperature was gradually raised to 305°C, and a polycondensation reaction was finally carried out at 13 Pa. The intrinsic viscosity of the polymer reached 0.5 dL/g 50 minutes after the beginning of the vacuum procedure, and 0.44 part of triphenyl phosphite was added at that point in time. A poly(1,4-cyclohexylene dimethylene terephthalate) (PCT) polymer was obtained by stirring under reduced pressure for five more minutes. Table 2 shows the intrinsic viscosity, polycondensation time, and COOH content of the PCT obtained.

Working Example 17

One hundred parts of dimethyl 2,6-naphthalenedicarboxylate, 50 parts of 1,4-butanediol, 0.06 part of tetrabutyl titanate, and 0.08 part of imidazole were placed in the same reactor as in Working Example 1. Transesterification was carried out while gradually raising the temperature from 140 to 230°C under normal pressure, and the methanol was distilled off. The supply of nitrogen was stopped, the reactor was then placed under vacuum while the temperature was gradually raised to 260°C, and a polycondensation reaction was finally carried out at 13 Pa. A

quantity of 0.34 part of triphenyl phosphite was added when the intrinsic viscosity of the polymer reached 0.5 dL/g, and a polybutylene-2,6-naphthalate (PBN) polymer was obtained by stirring under reduced pressure for five more minutes. Table 2 shows the intrinsic viscosity, polycondensation time, and COOH content of the PBN obtained.

[0010] Working Example 18

One hundred parts of dimethyl terephthalate, 60 parts of 1,4-butanediol, 0.06 part of tetrabutyl titanate, and 0.08 part of imidazole were polymerized in the same way as in Working Example 1, and a PBT polymer with an intrinsic viscosity of 0.65 dL/g was obtained 80 minutes after the beginning of the vacuum procedure. This polymer was removed from the reactor, pelletized, mixed with 1.1 part of triphenyl phosphite, and melt kneaded in an ordinary extruder. The intrinsic viscosity of the PBT obtained rose to 1.15 dL/g, and the COOH content was 11 mEq/kg.

Working Example 19

Polymerization was carried out in the same way as in Working Example 18, and a PBT polymer with an intrinsic viscosity of 0.81 dL/g was obtained 100 minutes after the beginning of the vacuum procedure. This polymer was removed from the reactor, pelletized, mixed with 1.1 part of triphenyl phosphite, and melt extruded in an ordinary extruder. The intrinsic viscosity of the PBT obtained rose to 1.24 dL/g, and the COOH content was 19 mEq/kg.

[0011] Comparative Examples 1 and 2

PBT polymers were produced in the same way as in Working Example 1, except that no organic base or organic phosphorus compound was used. Table 3 shows the intrinsic viscosity, polycondensation time, and COOH content of the PBT obtained.

Comparative Example 3

A PBT polymer was produced in the same way as in Working Example 1, except that the imidazole was not used and 1.1 part of triphenyl phosphite was used instead. Table 3 shows the intrinsic viscosity, polycondensation time, and COOH content of the PBT obtained.

Comparative Example 4

A PBT polymer was obtained in the same way as in Working Example 1, except that the triphenyl phosphite was not used and 0.23 part of imidazole was used instead. Table 3 shows the intrinsic viscosity, polycondensation time, and COOH content of the PBT obtained.

Comparative Example 5

An attempt was made to produce a PBT polymer in the same way as in Working Example 1, except that 0.23 part of imidazole and 1.1 part of triphenyl phosphite were added after the end of the transesterification reaction, i.e., before the polycondensation reaction. Little elevation of the molecular weight could be seen.

Comparative Example 6

A PBT polymer was produced in the same way as in Working Example 1, except that 0.008 part of imidazole and 0.04 part of triphenyl phosphite were used. Table 3 shows the intrinsic viscosity, polycondensation time, and COOH content of the PBT obtained.

Comparative Example 7

An attempt was made to produce a PBT polymer in the same way as in Working Example 1, except that 0.5 part of imidazole and 2.2 parts of triphenyl phosphite were used. However, the polymer could not be obtained because it solidified in the reactor due to secondary reactions.

Comparative Example 8

A PBT polymer was produced in the same way as in Working Example 1, except that 0.23 part of imidazole and 1.7 part of tridecyl phosphite instead of triphenyl phosphite were used. Table 3 shows the intrinsic viscosity, polycondensation time, and COOH content of the PBT obtained.

Comparative Example 9

A PET polymer was produced in the same way as in Working Example 14, except that no organic base or organic phosphorus compound was used. Table 3 shows the intrinsic viscosity, polycondensation time, and COOH content of the PET obtained.

Comparative Example 10

A PCT polymer was produced in the same way as in Working Example 16, except that no organic base or organic phosphorus compound was used. Table 3 shows the intrinsic viscosity, polycondensation time, and COOH content of the PCT obtained.

Comparative Example 11

A PBN polymer was produced in the same way as in Working Example 17, except that no organic base or organic phosphorus compound was used. Table 3 shows the intrinsic viscosity, polycondensation time, and COOH content of the PBN obtained.

[0012] Comparative Examples 12 and 13

Solid-phase polymerization was carried out at 205°C in a nitrogen stream using the PBT polymer pellets with an intrinsic viscosity of 0.65 dL/g produced in Comparative Example 1. Solid-phase polymerization had to be continued for 14 hours to obtain a polymer with an intrinsic viscosity of 1.15 dL/g (Comparative Example 12). When the PBT polymer pellets with an intrinsic viscosity of 0.85 dL/g produced in Comparative Example 2 were solid-phase polymerized in the same way, the intrinsic viscosity barely reached 1.2 dL/g in 30 hours (Comparative Example 13).

[0013]

[Table 1]

Working example	Organic base		Organic phosphorus compound		Polycondensation time (min)	Intrinsic viscosity (dL/g)		COOH content in PBT (mEq/kg)	Comments
	Type	Amount added	Type	Amount added		At time of P compound addition	PBT produced		
1	Im	0.08 part (10 mmol/kg)	TPP	0.35 part (10 mmol/kg)	85	0.65	0.79	8	
2	Im	0.11 part (15 mmol/kg)	TPP	0.52 part (10 mmol/kg)	85	0.65	0.89	12	
3	Im	0.23 part (30 mmol/kg)	TPP	1.1 part (30 mmol/kg)	85	0.65	0.91	11	Im/TPP added simultaneously during polycondensation
4	Im	0.23 part (30 mmol/kg)	TPP	1.1 part (30 mmol/kg)	55	0.43	0.70	9	
5	2MeIm	0.09 part (10 mmol/kg)	TPP	0.35 part (10 mmol/kg)	85	0.65	0.78	6	
6	NMIm	0.09 part (10 mmol/kg)	TPP	0.35 part (10 mmol/kg)	85	0.65	0.82	10	
7	Py	0.26 part (30 mmol/kg)	TPP	1.1 part (30 mmol/kg)	85	0.65	0.72	15	
8	IQN	0.15 part	TPP	0.35 part	85	0.65	0.75	20	

Working example	Organic base		Organic phosphorus compound		Polycondensation time (min)	Intrinsic viscosity (dL/g)		COOH content in PBT (mEq/kg)	Comments
	Type	Amount added	Type	Amount added		At time of P compound addition	PBT produced		
		(10 mmol/kg)		(10 mmol/kg)					
9	BPy	0.18 part (10 mmol/kg)	TPP	0.35 part (10 mmol/kg)	85	0.65	0.71	16	
10	TrAz	0.08 part (10 mmol/kg)	TPP	0.35 part (10 mmol/kg)	85	0.65	0.72	19	
11	Im	0.08 part (10 mmol/kg)	DPP	0.27 part (10 mmol/kg)	85	0.65	0.71	12	
12	Im	0.08 part (10 mmol/kg)	TPPA	0.37 part (10 mmol/kg)	85	0.65	0.70	12	
13	Im	0.08 part (10 mmol/kg)	TPP	0.35 part (10 mmol/kg)	85	0.65	0.76	13	Catalyst: n-butyltin acid

[0014]

[Table 2]

Working example	Type of polyester	Organic base		Organic phosphorus compound		Polycondensation time (min)	Intrinsic viscosity (dL/g)		COOH content in polyester (mEq/kg)	Comments
		Type	Amount added	Type	Amount added		At time of P compound addition	Polyester produced		
14	PET	Im	0.05 part (10 mmol/kg)	TPP	0.23 part (10 mmol/kg)	75	0.60	0.74	27	Catalyst: germanium dioxide
15	PET	Im	0.05 part (10 mmol/kg)	TPP	0.23 part (10 mmol/kg)	75	0.60	0.74	28	
16	PCT	Im	0.10 part (10 mmol/kg)	TPP	0.44 part (10 mmol/kg)	55	0.50	0.58	17	
17	PBN	Im	0.08 part (10 mmol/kg)	TPP	0.34 part (10 mmol/kg)	55	0.50	0.60	12	

[0015]

[Table 3]

Comparative example	Type of polyester	Organic base		Organic phosphorus compound		Polycondensation time (min)	Intrinsic viscosity (dL/g)		COOH content in polyester (mEq/kg)	Comments
		Type	Amount added	Type	Amount added		At time of P compound addition	Polyester produced		
1	PBT	—	—	—	—	80	—	0.65	30	
2	PBT	—	—	—	—	100	—	0.81	47	
3	PBT	—	—	TPP	1.1 part (30 mmol/kg)	85	0.65	0.66	25	
4	PBT	Im	0.23 part (30 mmol/kg)	—	—	85	—	0.68	27	
5	PBT	Im	0.23 part (30 mmol/kg)	TPP	1.1 part (30 mmol/kg)	180	—	—	—	TPP added before polycondensation: molecular weight did not rise
6	PBT	Im	0.008 part (1 mmol/kg)	TPP	0.04 part (1 mmol/kg)	85	0.65	0.68	25	
7	PBT	Im	0.5 part (60 mmol/kg)	TPP	2.2 part (60 mmol/kg)	80	—	—	—	Prominent secondary reactions
8	PBT	Im	0.23 part (30 mmol/kg)	TDP	1.7 part (30 mmol/kg)	85	0.65	0.65	25	
9	PET	—	—	—	—	115	—	0.76	44	Catalyst: germanium dioxide
10	PCT	—	—	—	—	70	—	0.57	35	
11	PBN	—	—	—	—	70	—	0.55	23	

[0016] Notes)

Im: imidazole

2MeIm: 2-methylimidazole

NMIm: N-methylimidazole

Py: pyridine

IQN: isoquinoline

BPy: 2,2-bipyridyl

TrAz: 1,2,4-triazole

TPP: triphenyl phosphite

DPP: diphenyl phosphite

TPPA: triphenyl phosphate

TDP: tridecyl phosphite

[0017]

[Merits of the Invention] The thermoplastic polyester obtained by the process of the present invention has a very low content of terminal carboxyl groups and excellent resistance to hydrolysis. Moreover, the present invention makes it possible to markedly shorten the polycondensation time and to omit the solid-phase polymerization step even when producing high-molecular-weight polyester. Therefore, the present invention makes it possible to provide high-quality polymers at a low cost.